Biomass to Gasoline (BTG): Upgrading Pyrolysis Vapors to Aromatic Gasoline with Zeolite Catalysis at Atmospheric Pressure

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ABSTRACT

The primary pyrolysis vapors generated by the fast pyrolysis of biomass at atmospheric pressures consist initially of low-molecular-weight compounds, but which polymerize readily upon condensation. Prior to condensation, these primary vapors have been found to be very reactive with ZSM-5 catalyst to produce methyl benzenes boiling in the gasoline range. This gasoline is predicted to have very high blending octane numbers. By-products are coke, carbon oxides, water, naphthalenes, ethylene, propylene, and some phenols. The effect of different by-products on the theoretical gasoline yield is examined. Preliminary results, generated with a reactor having a fixed bed of 100 g of catalyst, are examined for the continuous feeding of never-condensed primary vapors and compared to feeding methanol in the same reactor.

INTRODUCTION

The conversion of biomass materials to high octane gasoline has been actively pursued for many years. Historically, methanol was made in very low yields by the destructive distillation of hardwoods. More recently, the manufacture of methanol has been by the reaction of synthesis gas over catalysts at high pressures. In theory, any carbon source can be used for this catalytic generation of methanol, but in practice, biomass has not been advantageous relative to coal or natural gas. Other approaches to making liquid fuel from biomass have involved the fermentation of biomass to ethanol in a rather slow process, which produces a substantial amount of by-product solids and liquid wastes. The conversion of biomass to alcohols is technically feasible, but the utilization of the alcohols as transportation fuels will require modifications to the distribution systems and to the individual automobiles. The high-pressure liquefaction of biomass to oxygenated liquids followed by high-pressure catalytic hydrogenation to form hydrocarbons is one approach to convert biomass to liquid fuels (1). However, in the last decade, Mobil has developed the use of a zeolite catalyst for the conversion of methanol to gasoline (2). This process has recently been commercialized and is now in operation in New Zealand (3). The zeolite catalyst used in the Mobil process is a medium pore zeolite, which has shape selectivity to restrict the products to methylated benzenes, isoparaffins, and olefins, while preventing the formation of coke in the catalyst pores (4). This catalyst is known as ZSM-5, and its commercial use is controlled by Mobil.

The reactivity of high-molecular-weight vegetable oils with ZSM-5 was reported in 1979 (5) and, in fact, ZSM-5 catalyst is very reactive toward most small oxygenated species to convert them to methylated benzenes and other products (6, 7). Although alcohols appear to be some of the best feedstocks for ZSM-5 catalysis due to their low coking tendencies, the petroleum industry has long made use of zeolite catalysts for the cracking of very heavy hydrocarbons to produce gasoline and about 5 to 15 weight percent coke. This suggests that the formation of coke and the need for frequent catalyst regeneration will heavily impact the reactor design, but that significant coke formation can be part of a viable commercial process. The thrust

of this paper is to examine possible stoichiometries and preliminary experimental results from using primary pyrolysis vapors made by the fast pyrolysis of sawdust at atmospheric pressure in a vortex reactor. The production of these oxygenate vapors is addressed in a companion paper (8).

STOICHIOMETRY

Although the hydrocarbon products have an unusual feedstock independence, the chemistry involved with different feedstocks over the ZSM-5 catalyst varies considerably with the functionality of the oxygen in the feedstock. As seen in Table 1, the hydroxy and methoxy groups in general have a very strong tendency to reject oxygen in the form of water, as seen for the case of methanol, dimethyl ether (9), glycerol (10), and phenols (11). Rejection of the oxygen as carbon monoxide occurs preferentially to water in a 4:1 ratio with furfural (7, 10). The reaction of n-butyl formate over ZSM-5 produces equal molar amounts of water and carbon monoxide (9). Acetic acid reacts to produce acetone, water, and carbon dioxide with only small amounts of carbon monoxide. The reaction of acetone produces largely water as the oxygen-containing by-product. The acetate group appears to decompose in such a way as to reject four times as much oxygen as carbon dioxide than as carbon monoxide, but with over 50% of the oxygen rejected in the form of water (12). Glucose and starch were reported to reject oxygen preferentially as water rather than as carbon monoxide in a 3-1/2 to 1 ratio with very little formation of carbon dioxide. Sucrose and xylose also produced very little carbon dioxide, but favored the formation of water over carbon monoxide by only 1-1/2 to 1 (7), perhaps due to the formation of some furfural as part of the intermediates. In summary, hydroxyl and methoxy groups tend to reject oxygen in the form of water; aryl ethers reject a nearly equal amount of oxygen in water and carbon monoxide; carbonyl and formate groups reject oxygen largely as carbon monoxide, and carboxyl groups reject oxygen mostly as carbon dioxide and water. With the model compounds listed in Table 1, many of these trends may also be a function of reaction conditions as well as reactants. A model compound study coupled with a process variable study is in progress at SERI with the free-jet, molecular beam/mass spectrometer (FJMBMS) (13).

The method of oxygen rejection which occurs over the catalyst has a very important impact on the potential yield of hydrocarbons, especially for a feedstock like biomass which has a relatively low hydrogen content. Although the products formed from a few compounds reacted with ZSM-5 are known for certain conditions, methods to manipulate the by-product slate are essentially unexplored. However, the desirability to reject oxygen as carbon oxides becomes quite obvious by examining potential product slates which are possible from the stoichiometry of the reacting primary pyrolysis vapors, $CH_{1.2}O_{0.49}$. Based on the assumption of a 70 wt % yield of primary vapors, Table 2 shows that of the product slates considered, the best hydrocarbon yields would be attained with oxygen rejection as carbon dioxide, and the excess hydrogen used to also reject oxygen as water. Note that the liquid hydrocarbon product assumed corresponds to xylene, C_8H_{10}, rather than to more hydrogen-rich hydrocarbons such as olefins, C_nH_{2n} (as will be discussed, the liquid hydrocarbon products actually made from these pyrolysis vapors are aromatic in nature). If carbon monoxide is the assumed carbon oxide, more carbon is needed to reject the oxygen, which decreases the potential hydrocarbon yields, as shown by reaction (2) of Table 2. If the by-product gases are a mixture of carbon oxides, methane, olefins, etc., as shown empirically in reaction (3) as $CH_{0.65}O_{0.82}$, then the gasoline yields would be lowered due to the noncondensible hydrocarbons. The formation of pure carbon could still result in considerable gasoline yields as shown by reaction (4). However, since coke formation is typically an aromatization reaction to produce polycyclic aromatic hydrocarbons containing residual hydrogen, reaction (5) is probably the more reasonable coking reaction to expect, which

produces water and coke but no gasoline at all. In summary, the more desired reactions produce carbon oxides and water as by-products. Undesired reactions produce noncondensible hydrocarbons and/or coke and water.

EXPERIMENTAL

The primary pyrolysis vapors, used as feedstock, were produced by fast pyrolysis in a vortex reactor from coarse softwood sawdust, as discussed in reference (8). After the vapors left the vortex reactor system, they were allowed to cool to the desired catalytic reaction temperature, as they passed through a tubular transfer line to the catalytic reactor. The transfer line was located inside of a series of six tubular furnaces, which allowed the vapor stream to equilibrate to the desired temperature. The residence time of the vapor in the transfer line was about one-half second prior to reaching the 2.5-cm diameter catalytic reactor shown in Figure 1. The catalytic reactor had a 30-cm-long fixed bed of 100 g of ZSM-5 containing catalyst (MCSG-2), which was located in the middle of the sixth furnace section. The catalyst was in the form of 1.4-mm diameter extrudate and supplied by Mobil Research and Development Corp. in a cooperative agreement with the Solar Energy Research Institute. The temperature of the catalyst bed was measured with an axial thermocouple inside a 6-mm thermowell. The temperature profile of the bed was determined by moving the axial thermocouple within the thermowell. A sintered stainless steel filter rated at 5 micrometers was used to remove char fines from the pyrolysis vapors. The products were collected in water-cooled condensers. The pressure in the reactor was slightly above the local atmospheric pressure at about 95 kPa. Analysis of the organic condensates was with a 5-micrometer wide bore capillary column having a length of 60 m. The capillary column was coated with one micrometer of cross-linked methyl silicones. With helium as the carrier gas, the temperature profile started at $0^{\circ}C$ for 4 minutes, followed by a temperature ramp of $8^{\circ}C/min$ until a temperature of $260^{\circ}C$ was reached. Detection of the eluted organics was by flame ionization detection (FID). Identification of the major peaks was by reference materials, whereas the minor peaks were identified by a combination of the FJMBMS at SERI and a GC/MS located in the Department of Chemical and Petroleum-Refining Engineering of the Colorado School of Mines. The noncondensible gases were analyzed with a Carle GC designed for refinery gas analysis, which used thermal conductivity detection (TCD) and was calibrated with a gravimetrically prepared reference mixture. Electronic grade methanol (99.9% pure) was used for comparison to the softwood feedstock.

EXPERIMENTAL RESULTS

Methanol. To verify the activity of the catalyst and to gain experience in the operation of the catalyst system, methanol was metered into a preheater tube located inside of the transfer line heated to $500^{\circ}C$. This preheating proved to .be too severe and the products which emerged from the catalytic reactor were dominated by hydrogen and carbon monoxide in a 2:1 ratio, as shown in Table 3. This would be expected from thermal decomposition of the methanol prior to reaching the catalyst. This experiment was repeated using a preheating temperature ramp to just reach $400^{\circ}C$ at the entrance to the catalytic reactor. The catalytic reactor was held at a nominal $400^{\circ}C$ prior to the addition of the methanol at a space velocity (WHSV) of 0.9 g methanol per gram of catalyst. The noncondensible gas composition is shown in Table 3 and was rich in hydrogen and alkanes (methane, propane, and isobutane). The gaseous olefins would be used to akylate the reactive isobutane to result in a highly branched-chain gasoline fraction (14). The GC for the hydrocarbon liquid is shown in Figure 2a; the liquid product contained relatively little alkanes or olefins and was dominated by methylated benzenes, such as toluene, xylenes, and trimethyl benzenes. Relatively very small amounts of naphthalenes were

seen. The temperature profile of the catalytic reactor immediately prior to and also during this experiment is shown in Figure 3. The location of the temperature-profile maxima was quite stable, which indicates that the catalyst was not significantly deactivating during the short time of the experiment. This low rate of catalyst deactivation is consistent with data published by Mobil personnel (15). The ratio of gasoline to water in the condensates suggests that the gasoline yield was only about one-third of the potential due to the formation of the noncondensible hydrocarbons. This product slate is in general agreement with data reported by Mobil for the reaction conditions (15).

Primary Pyrolysis Vapors. After a catalyst regeneration cycle to remove residue from the methanol experiments, a slipstream of the primary pyrolysis vapors were passed over the ZSM-5 catalyst using steam as the carrier gas at a weight ratio of two parts of steam to one part of wood feed. The pyrolysis vapors were cooled from $510^{\circ}C$ at the exit of the vortex reactor to $400^{\circ}C$ at the entrance of the catalytic reactor. Figure 4 shows the temperature profile immediately prior to feeding the biomass, as well as 5-10 minutes later. The temperature profile with pyrolysis vapors as feed was not as large in magnitude as that seen with methanol and it had a very broad maximum. The heat of reaction of the pyrolysis vapors is less exothermic than for methanol and the steam carrier gas also has a moderating effect on the temperature rise. The broadness of the temperature profile reflects that the pyrolysis vapors are a complex mixture of compounds, which are probably reacting at different rates. The broader and lower temperature profile would make temperature control easier in a biomass-to-gasoline (BTG) reactor than in a methanol-to-gasoline (MTG) reactor. The location of the temperature maximum was monitored during the run, as shown in Figure 5. During the fairly short experiment, the temperature maximum was observed to move to the end of the reactor, indicating a fairly rapid deactivation of the catalyst had occurred. During this time, the composition of the hydrocarbon products appeared to be relatively constant. The GC chromatogram of the liquid hydrocarbons is shown in Figure 2b for comparison to the products made from methanol. As can be seen by inspection of the two gas chromatograms, the gasoline fraction (eluting before naphthalene) made from wood is very similar to that made from methanol. The composition of the gas formed over the catalyst from the pyrolysis vapors is shown in Table 3, as calculated from tracer gas concentrations before and after the reactor, along with the gas composition formed by the thermal decomposition of the pyrolysis vapors as determined previously (16); the catalytically formed gases had significantly less hydrogen and methane, but more carbon dioxide and propylene than the thermally formed gases. In comparing the composition of the gases formed by the catalytic conversion of the pyrolysis vapors to the catalytic conversion of the methanol, the relative hydrogen richness of the methanol becomes apparent in the relatively high hydrogen, methane, propane, and isobutane yields. The relative hydrogen richness is summarized by the empirical formulas for the two gas streams, in which the hydrogen-to-carbon ratio for the wood-derived gases is one-fourth that for the methanol-derived gases. This excessive amount of hydrogen in the methanol-derived gases suggests that methanol could be used as a hydrogen donor to hydrogen-poor feedstocks and this has been explored by several researchers (7, 10-12). The very low yield of isobutane from pyrolysis vapors would preclude the use of alkylation to incorporate the ethylene, propylene, and butenes into the gasoline product with a standalone process. Adsorption of the gaseous olefins onto cold ZSM-5 at low pressures may be a viable method to recycle them into the catalytic reactor. A comparison of Tables 2 and 3 reveals that the empirical gas composition calculated to have been made catalytically from the pyrolysis vapors corresponds to reaction (3), which has a thermal efficiency of 57%. However, the laydown of coke on the catalyst would serve to compete for the pyrolysis vapor feedstock and reduce the gasoline yields by reaction (5) as previously discussed. The quantitation of the coke is in progress.

DISCUSSION

Pyrolysis vapors made by the fast pyrolysis of softwood are very reactive with ZSM-5 catalyst to form a liquid hydrocarbon product, which is very similar to that formed from methanol. Although the catalyst is deactivated relatively quickly with pyrolysis vapors compared to methanol, other experimentation we have performed indicates that the catalyst can be oxidatively regenerated. This suggests that a catalytic reactor, which can maintain a high level of catalytic activity in spite of high coking rates, would be desired. This problem has been addressed and resolved by the petroleum refining industry which utilizes an entrained-bed reactor (riser-cracker), to crack heavy hydrocarbons to gasoline and about 5% to 15% coke, coupled with a fluidized-bed oxidative regenerator for the relatively slow, controlled oxidative coke combustion and catalyst regeneration (17). For the conversion of biomass to gasoline, these preliminary data are quite encouraging that a nearly direct conversion of biomass to gasoline can be accomplished at atmospheric pressures in one very rapid thermal cycle without the cost of hydrogen manufacture. With the calculated thermal efficiencies, it appears that there will be sufficient energy in the by-products to operate the process, even including the drying of a rather wet biomass feedstock prior to pyrolysis.

The gasoline product is almost entirely methylated benzenes with only a small amount of benzene. This gasoline would be expected to have octane ratings in excess of 100 and to have blending octane numbers between 115 and 135 based on reported blending octane values for the various methylated benzenes (18). Due to the expected continued demand for unleaded gasoline having higher octane numbers, the gasoline made from biomass by this process would be expected to command premium prices if sold to a petroleum refinery for blending purposes. The naphthalenic fraction of the organic products could easily be hydrocracked to increase the gasoline yields in a modern refinery (19). At this time, the phenolic by-products appear to be present in minor amounts and probably will not warrant recovery.

SUMMARY

The conversion of primary pyrolysis vapors made from biomass is a relatively new research and development area which is showing early promise. The extent to which the product slate can be manipulated by process variables will impact heavily on the viability of this process.

ACKNOWLEDGEMENTS

REFERENCES

(1)   Baker, E. G. (1987), ACS Symposium on Production, Analysis, and Upgrading of Pyrolysis Oils from Biomass, Denver, CO, April 5-10.

(2)   Meisel, S. L.; McCullough, J. P.; Lechthaler, C. H.; Weiz, P. B. (1976), CHEMTECH, February, 86-89.

(3)   Anon, 1986, Chemical Engineering, March 3, p. 10.

(4)   Dejaive, P.; Auroux, A.; Gravelle, P. C.; Vedrine, J. C. (1981), J. Cat., 70, 123-136.

(5)   Weisz, P. B.; Haag, W. O., and Rodewald, P. G (1979), Science, 206, 5 October, 57-58.

(6)   Diebold, J. P.; Chum, H. L.; Evans, R. J.; Milne, T. A.; Reed, T. B.; Scahill, J. W. (1986), Proceedings of Energy from Biomass and Wastes X, IGT/CBETS, Washington, D.C., April 7-10.

(7)   Chen, N. Y.; Degnan, T. F., Jr.; Koenig, L. R. (1986), CHEMTECH, August, 506-511.

(8)   Diebold, J. P.; and Scahill, J. W. (1987), ACS symposium on Production, Analysis, and Upgrading of Pyrolysis Oils from Biomass, Denver, CO, April 5-10.

(9)   Chang, C. D.; and Silvestri, A. J. (1977), J. Cat. 47, 249-259.

(10) Hanniff, M. I.; and Dao, L. H. (1986), Proceedings of Energy from Biomass and Wastes X, IGT/CBETS, Washington, D.C., April 7-10.

(11) Chantal, P. D.; Kaliaguine, S.; and Grandmaison, J. L. (1985), Appl. Cat., 18, 133-145.

(12) Chang, C. D.; Chen, N. Y.; Koenig, L. R.; and Walsh, D. E. (1983), preprints of 185th ACS Meeting, Div. of Fuel Chem., Seattle, WA, March 20-25, 146-152.

(13) Evans, R. J.; and Milne, T. A. (1986), private communication, October.

(14) Kam, A. Y.; and Lee, W. (1978), Fluid Bed Process Studies on Selective Conversion of Methanol to High-Octane Gasoline, Mobil Research and Development Corp., U.S. DOE Contract No. EX-76-C-01-2490 FE-2490-15.

(15) Chang, C. D. (1983), Hydrocarbons from Methanol, Marcel Dekker, NY.

(16) Yurchak, S.; Voltz, S. E.; and Warner, J. P. (1979), Ind. Eng. Chem. Process. Des. Dev., 18, No. 3, 527-534.

(17) Diebold, J. P. (1985), Thesis T-3007, Colorado School of Mines, Golden, CO 80401.

(18) Decroocq, D. (1984), Catalytic Cracking of Heavy Petroleum Fractions, Gulf Publishing Company, Houston, TX.

(19) Lovell, W. G. (1948), Ind. Eng. Chem., 40, No. 12, 2388-2438.

(20) Gary, J. H.; and Handwerk, G. E. (1975), Petroleum Refining, Technology, and Economics, Marcel Dekker, NY, pp. 121-141.

Table 1. Reported Distribution of Oxygen in Inorganic By-Products with Various Feedstocks over ZSM-5 Catalyst

Compound	Oxygen Radical in Reactant*	% of Oxygen in By-Products			
		H_2O	CO	CO_2	Reference
methanol	H, M	100	--	--	(8)
dimethyl ether	E, M	100	--	--	(8)
guiacol	H, M	96	3	1	(10)
glycerol	H	92	7.5	0.5	(9)
xylenol	H	93	6	1	(10)
eugenol	H, M	89	9	2	(10)
anisole	M	88	12	tr	(10)
2,4 dimethyl phenol	H	87	12	1	(10)
o-cresol	H	80	17	3	(10)
starch	H, E	78	20	2	(7)
isoeugenol	H, M	77	19	4	(10)
glucose	Cl, H, E	75	20	5	(6)
dimethoxymethane	M, E	73	6	21	(8)
xylose	Cl, H, E	60	35	5	(6)
sucrose	H, E	56	36	8	(6)
n-butyl formate	C2	54	46	0	(8)
diphenyl ether	E	46	46	8	(10)
furfural	Cl, E	14-22	75-84	2.5-3.0	(6, 9)
methyl acetate	C2	54	10	36	(11)
acetic acid	C2	50	4	46	(11)

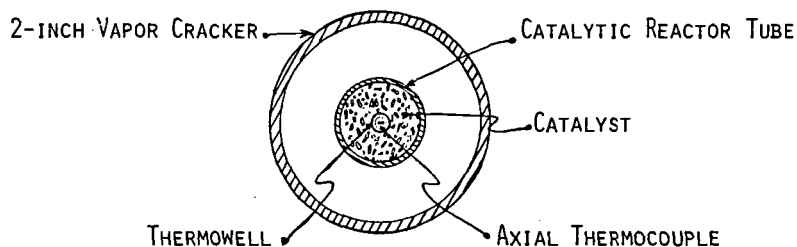*H = hydroxy; M = methoxy; E = C-O-C; Cl = carbonyl; C2 = carboxy

FIGURE 1. CROSS SECTIONAL VIEW OF THE FIXED-BED CATALYTIC REACTOR.

Table 2. Stoichiometric Relationships of By-Products to Gasoline Yields using Primary Softwood Pyrolysis Vapors as the Feedstock

Assumed Reaction	U.S. Gal Gasoline* Ton Dry Wood	Wt Gasoline* Wt Wood	Energy in Gasoline* Energy in Wood
1) $CH_{1.2}O_{0.49} \rightarrow 0.100\ C_8H_{10} + 0.20\ CO_2 + 0.10\ H_2O$	99	0.35	0.75
2) $CH_{1.2}O_{0.49} \rightarrow 0.085\ C_8H_{10} + 0.32\ CO + 0.23\ H_2O$	84	0.30	0.64
3) $CH_{1.2}O_{0.49} \rightarrow 0.073\ C_8H_{10} + 0.42\ CH_{0.65}O_{0.82} + 0.10\ H_2O$	75	0.27	0.57
4) $CH_{1.2}O_{0.49} \rightarrow 0.022\ C_8H_{10} + 0.824\ C + 0.49\ H_2O$	22	0.08	0.17
5) $CH_{1.2}O_{0.49} \rightarrow CH_{0.22} + 0.49\ H_2O$ ("coke")	0	0	0

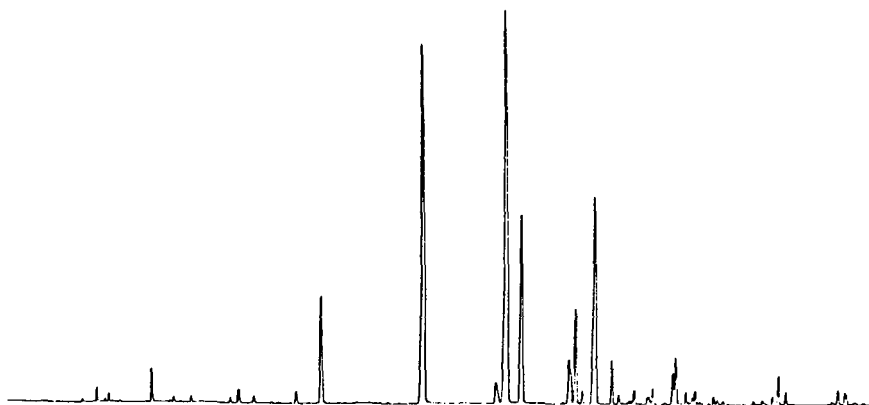*Yields reflect an assumed 70 wt % conversion of softwood to primary pyrolysis vapors.

FIGURE 2A. GC OF HYDROCARBON PRODUCTS MADE FROM METHANOL
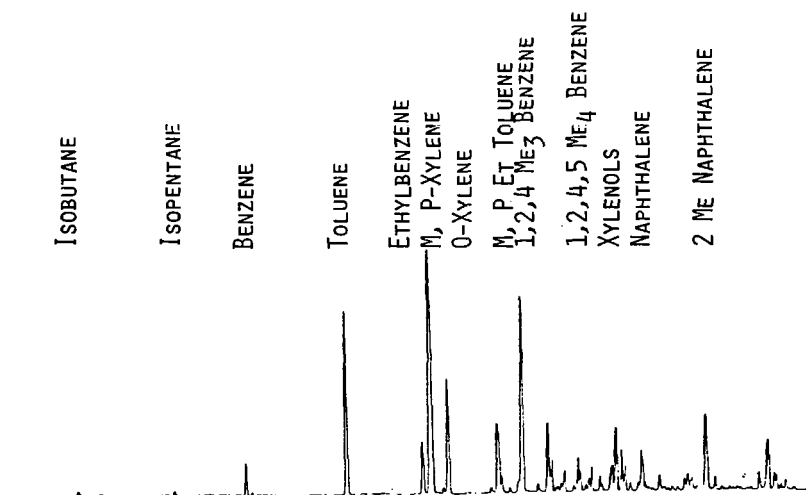AT 400°C WITH ZSM-5 CATALYST

FIGURE 2B. GC OF HYDROCARBON PRODUCTS MADE FROM SOFTWOOD
PRIMARY PYROLYSIS OIL VAPORS AT 400°C WITH
ZSM-5 CATALYST

Table 3. Calculated Molar Compositions of Net Product Gases
(ZSM-5 containing catalyst - Mobil's MCSG-2)

Feed	Softwood Pyrolysis Vapor $(CH_{1.2}O_{0.49})$		(CH_4O) Methanol	
Reactor	Thermal (Run 55)	Catalytic (Run 76-C)	Thermal (Run 74-C)*	Catalytic (Run 75-C)
H_2	10.6	-0.6	62.8	18.4
CO	59.4	69.8	31.1	4.4
CO_2	5.6	15.2	1.4	2.8
CH_4	12.2	1.4	2.1	16.2
C_2H_2	0.5	--	--	--
C_2H_4	5.3	5.0	1.6	5.3
C_2H_6	1.1	0.3	0.3	4.1
C_3H_6	1.9	6.0	0.7	5.3
C_3H_8	--	0.5	0.4	17.8
C_4H_8	1.1	1.2	--	2.3
$iso-C_4H_{10}$	--	0.2	0.1	14.4
$n-C_4H_{10}$	--	--	--	5.3
C_5+	2.4	--	--	3.6
Empirical Formula	$CH_{1.3}O_{0.65}$	$CH_{0.65}O_{0.82}$	$CH_{3.6}O_{0.8}$	$CH_{2.7}O_{0.05}$

*In this run, the methanol is thought to have thermally decomposed for the most part prior to reaching the catalyst.
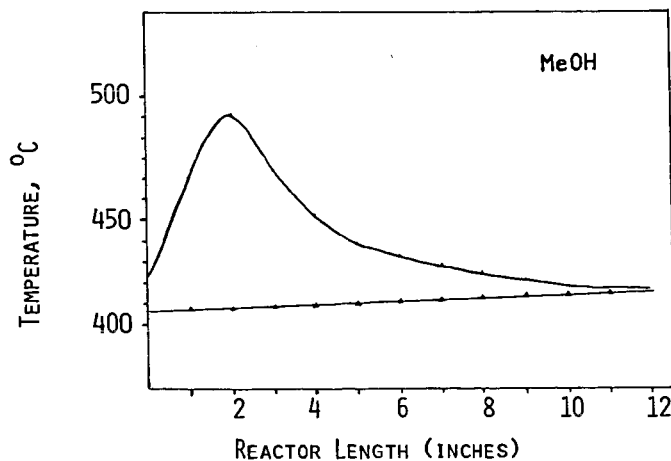

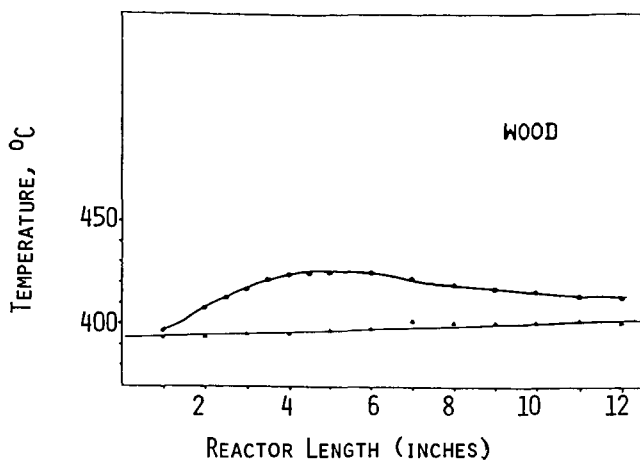FIGURE 3. TEMPERATURE PROFILE FOR METHANOL REACTANT

FIGURE 4. TEMPERATURE PROFILE FOR SOFTWOOD PYROLYSIS
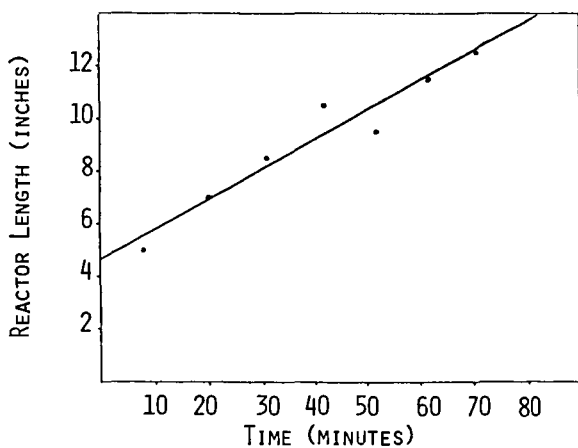VAPORS AS THE REACTANTS

FIGURE 5. LOCATION OF THE MAXIMUM CATALYST BED TEMPERATURE,
SHOWING CATALYST DEACTIVATION